Le Tour 2006: Daily Analysis Report

Stage 13: Beziers Mediterrandee to Montelimar, 230 km Saturday, July 15th

Floyd Landis

Temp: 95 °F / 35 °C Humidity: 60 % Heat Index: 113 °F / 45.05 °C

Stage Results: 230.0 km 38.9 km/h 24.1 mph

GC Results 3,440.0 km ridden 40.8 km/hr 25.3 mph

Place: 29 Time: 5 hrs 54 min 33 sec Gap: 29 min 57 sec

Place: 2 Time: 59 hrs 52 min 3 sec Gap: 0 hrs 1 min 2 sec

Race Notes: It was so freaking hot today. Way too hot to do anything except nothing. Why was it so hot. Peirero and Voight and Chavenal, and some other guy got away and built a 30 minute gap. Floyd gives up yellow. Super easy. That's a good thing. Time to get some rest the next two days.

Power, RPE, Heart Rate, Work, RPE vs. Power, HR vs. Power:

		Power when Moving		Power when Pedaling		Strain		Work or Stress in Kjoules From:			RPE	HR
		Watts	Watts/kg	Watts	Watts/kg	RPE	HR	Power	RPE	HR	Pwr	Pwr
Rider	Today	**178**	**2.56**	**217**	**3.12**	**5**	**NA**	**3,787**	**5,683**	**NA**	**1.50**	**NA**
	Tour Avs	218	3.14	266	3.84	4.5	NA	3,926	4,528	NA	1.13	NA
	Tour Min	178	2.56	217	3.12	3.5	NA	2,624	2,682	NA	1.01	NA
	Tour Max	267	3.84	314	4.52	7	NA	5,870	7,619	NA	1.50	NA
2005	Today						NA			NA		NA
	Tour Avs	223	3.28	268	3.94	6.3	NA	3,911	5,348	NA	1.34	NA
	Tour Min	164 (S21)	2.41	214	3.15	4	NA	2,174 (S21)	2,651 (S21)	NA	0.88	NA
	Tour Max	285 (S11)	4.19	314	4.62	10 (S15)	NA	5,620 (S15)	11,286 (S15)	NA	2.01	NA

Power Distribution:

		Zero Watts		Per Kilogram of Body Weight																				Relative to RPE (1-10)					
				Time (%)										Time (min)										Time (%)			Time (min)		
		%	min	0-1	1-2	2-3	3-4	4-5	5-6	6-7	7-8	8-9	>9	0-1	1-2	2-3	3-4	4-5	5-6	6-7	7-8	8-9	>9	<H	H	>H	<H	H	>H
Rider	Today	17.8	63.0	24.4	16	19.3	18	12	5.4	2.4	1.1	0.4	0.6	86	57	68	64	42	19	8	4	1	2	78	17	4	276.5	61.6	15.9
	Tour Avs	18	55.0	23.1	13	14.5	14	14	10.8	6.09	2.81	1.3	1.2	69	36	42	42	43	34	18	8.2	3.7	3.5	64	24.5	11	189.9	76.05	33.51
	Tour Min	13.4	29.0	17.2	5.5	7.9	10	9.8	5.4	2.4	1.1	0.4	0.6	44	20	29	31	21	15	8.5	3.9	1.4	2.1	42	16.7	4.5	154.5	35.91	15.93
	Tour Max	23.9	80.0	30	19	19.3	18	24	21.3	9.4	3.8	1.7	1.7	101	57	68	64	89	78	29	11	5	5	78	45.5	16	276.5	166.5	47.95
2005	Today																												
	Tour Avs	15	41.2	20.4	11	12.4	14	16	14	7.22	2.91	1.2	1.1	55	29	34	38	45	40	20	8	3	3						
	Tour Min		26.0	12.6	5.7	6.9	11	9.1	6.8	3.7	1.7	0.9	0.7	37	16	19	26	20	15	8	4	2	2						
	Tour Max		84.0	33.8	16	16.8	17	23	27.9	10.3	4.7	1.7	1.7	104	42	46	48	73	85	31	14	5	5						

Peak Power Output: 5 min 3.32 W/kg 30 min 3.96 W/kg

		Average Power (watts)								Distance from Start (km)								# of surges > than w/kg of:		
		Sec		Min				Hour		Sec		Min				Hour				
		5	30	1	5	10	30	1	2	5	30	1	5	10	30	1	2	> 6	> 8	> 10
Rider	Today	833	569	471	340	296	269	223	n	181	6.4	6.1	3.7	175	158	14.3	n	201	49	14
	Tour Avs	894	622	529	414	360	305	275	n								n	373	101	29
	Tour Min	825	528	471	340	296	252	214	n								n	201	49	14
	Tour Max	972	912	674	465	426	377	346	n								n	487	141	43
2005	Today																			
	Tour Avs	841	555	479	400	360	314	283	255											
	Tour Min	731	465	403	308	283	249	231	193											
	Tour Max	965	645	555	478	435	386	359	315											

Surges:

Hydration & Energy Status:

Weight (kg)				Bottle Count	Sweat Loss (l)
Pre	Post	Δ	% Δ		
69	67	2	2.8986	20	11.6
Est Loss (l)	Sweat Rates			% GME	Kcals
	l/hr	l/mjoule			
5.12	1.96	3.06		24	3769.509476

Race Food Eaten:

Climbs and Special Features: Total Elevation Gain: NA meter NA feet Cr 0.005 k 0.18 Bike Wt 7 Wt 68 75

Climb/Feature:	Start (km)	Top (km)	Total Dist	% Grade	Calc Grade	Start Elev	Top Elev	Total Gain	Time		Speed km/hr	VAM m/hr	Estimated Power				Actual		% Diff
									Min	Sec			Roll	Aero	Grav	Total	Power	w/kg	
1. Cote de Puechabon	54.9	57.5	2.6	5.2	5.201252	154.95	290	135.05	7	13	21.61663	1123	23	40	236	299	280	4.03	6.42824401
2. Col de la Cardonille	75.3	77.5	2.2	5.5	5.5014885	209.15	330	120.85	5	4	26.05263	1431	27	70	301	399	312	4.49	21.78233629
3. Cote de l'Arbousset	118	119.5	1.5	4.5	4.5012197	162.55	230	67.45	3	29	25.83732	1162	27	68	245	340	306	4.40	10.0611583
4. Cote de Saint-Maurice	194.4	195.5	1.1	4.6	4.6003146	255.45	306	50.55	2	42.54	24.36323	1120	26	57	236	319	305	4.39	4.310480826
5. Cote de Villeneuve de Berg	203.1	205	1.9	5.3	5.3021742	291.4	392	100.6	4	48	23.75	1258	25	53	265	343	319	4.59	6.972182749
* All climbs were cat 4's.																			

Le Tour 2006: Daily Analysis Report

Stage 14: Montelimar to Gap, 180.5 km — **Sunday, July 16th**

Floyd Landis

Temp: 90 °F / 32 °C Humidity: 60 % Heat Index: 99.7 °F / 37.6 °C

Stage Results: 180.5 km 42.6 km/hr 26.4 mph

Place: 30 Time: 4 hrs 14 min 30 sec Gap: 0 min 7 sec

GC Results: 2,630.0 km ridden 40.9 km/hr 25.2 mph

Place: 2 Time: 64 hrs 5 min 4 sec Gap: 0 hrs 1 min 29 sec

Race Notes: Very hard stage. Lots of attack. First hour was ripping. Breakaway that was held to 5 minutes for most of the race. Strung out and going most of the day. Lots of riders off the back.

Power, RPE, Heart Rate, Work, RPE vs. Power, HR vs. Power:

		Power when Moving		Power when Pedaling		Strain		Work or Stress in Kjoules From:			RPE	HR
		Watts	Watts/kg	Watts	Watts/kg	RPE	HR	Power	RPE	HR	Pwr	Pwr
Rider	Today	**265**	**3.81**	**313**	**4.50**	**6**	**NA**	**4,047**	**4,686**	**NA**	**1.16**	**NA**
	Tour Avs	221	3.19	269	3.88	4.63	NA	3,934	4,539	NA	1.13	NA
	Tour Min	178	2.56	217	3.12	3.5	NA	2,624	2,682	NA	1.01	NA
	Tour Max	267	3.84	314	4.52	7	NA	5,870	7,619	NA	1.50	NA
[illegible]	Today						NA			NA		NA
	Tour Avs	223	3.28	268	3.94	6.3	NA	3,911	5,348	NA	1.34	NA
	Tour Min	164 (S21)	2.41	214	3.15	4	NA	2,174 (S21)	2,651 (S21)	NA	0.88	NA
	Tour Max	285 (S11)	4.19	314	4.62	10 (S15)	NA	5,620 (S15)	11,286 (S15)	NA	2.01	NA

Power Distribution:

		Zero Watts		Per Kilogram of Body Weight																				Relative to RPE (1-10)					
				Time (%)										Time (min)										Time (%)			Time (min)		
		%	min	0-1	1-2	2-3	3-4	4-5	5-6	6-7	7-8	8-9	>9	0-1	1-2	2-3	3-4	4-5	5-6	6-7	7-8	8-9	>9	<H	H	>H	<H	H	>H
Rider	Today	15.3	39.0	18.5	6.7	10	15	18	13.2	8.5	4.7	2.4	2.5	47	17	25	39	46	34	22	12	6	6	51	31	18	128.5	79.5	46
	Tour Avs	17.8	54.0	22.7	12	14	14	14	11	6.28	2.95	1.4	1.3	68	35	41	42	43	34	18	8.4	3.9	3.7	63	25	12	185.8	76.28	34.35
	Tour Min	13.4	29.0	17.2	5.5	7.9	10	9.8	5.4	2.4	1.1	0.4	0.6	44	**17**	**25**	31	21	15	8.5	3.9	1.4	2.1	42	16.7	4.5	**129**	35.91	15.93
	Tour Max	23.9	80.0	30	19	19.3	18	24	21.3	9.4	**5**	**2.4**	**3**	101	57	68	64	89	78	29	**12**	**6**	**6**	78	45.5	16	276.5	166.5	47.95
[illegible]	Today																												
	Tour Avs	15	41.2	20.4	11	12.4	14	16	14	7.22	2.91	1.2	1.1	55	29	34	38	45	40	20	8	3	3						
	Tour Min		26.0	12.6	5.7	6.9	11	9.1	6.8	3.7	1.7	0.9	0.7	37	16	19	26	20	15	8	4	2	2						
	Tour Max		84.0	33.8	16	16.8	17	23	27.9	10.3	4.7	1.7	1.7	104	42	46	48	73	85	31	14	5	5						

Peak Power Output:

5 min: 4.30 W/kg 10 min: 4.91 W/kg

Surges:

		Average Power (watts)								Distance from Start (km)								# of surges > than w/kg of:		
		Sec		Min				Hour		Sec		Min				Hour				
		5	30	1	5	10	30	1	2	5	30	1	5	10	30	1	2	> 6	> 8	> 10
Rider	Today	892	567	536	443	418	336	305	n	63	11.1	11	11	9.2	156	2.8	n	498	188	50
	Tour Avs	894	618	530	417	364	307	277	n								n	381	107	31
	Tour Min	825	528	471	340	296	252	214	n								n	201	49	14
	Tour Max	972	912	674	465	426	377	346	n								n	**498**	**188**	**50**
[illegible]	Today																			
	Tour Avs	841	555	479	400	360	314	283	255											
	Tour Min	731	465	403	308	283	249	231	193											
	Tour Max	965	645	555	478	435	386	359	315											

Hydration & Energy Status:

Weight (kg)				Bottle Count	Sweat Loss (l)
Pre	Post	Δ	% Δ		
69	68	1	1.4493	15	8.2
Est Loss (l)	Sweat Rates		% GME	Kcals	
	l/hr	l/mjoule			
5.47	1.93	2.03	24	4028.308648	

Race Food Eaten:

Climbs and Special Features:

Total Elevation Gain: 0 meter 0 feet Cr 0.005 k 0.18 Bike Wt 7 Wt 68.5 75.5

Climb/Feature:	Start (km)	Top (km)	Total Dist	% Grade	Calc Grade	Start Elev	Top Elev	Total Gain	Time Min	Time Sec	Speed km/hr	VAM m/hr	Estimated Power Roll	Estimated Power Aero	Estimated Power Grav	Estimated Power Total	Actual Power	Actual w/kg	% Diff
1. Cote du Bois-de-Salles	8.9	14	5.1	4.2	4.1997773	230	444	214	9	8	33.50365	1406	35	149	296	480	430	6.19	10.49385033
2. Col de Peyruergue	67	72.5	5.5	4.8	4.8000657	556.3	820	263.7	14	4	23.45972	1125	25	51	237	313	273	3.93	12.70533595
3. Col de Perty	88.2	97	8.8	5.1	5.0998007	854.8	1303	448.2	23	37.5	22.34921	1138	24	44	240	307	300	4.32	2.431261394
4. Cote de la Sentinelle	165.7	171	5.3	5	5.0005801	716.3	981	264.7	11	31.74	27.58262	1378	29	83	290	402	407	5.86	-1.164510382
5 Attacks > 10 w/kg on last climb																			
16 attacks > 8 w/kg on last climb																			

Le Tour 2006: Daily Analysis Report

Stage 15: Gap to L'Alpe d'Huez, 187 km **Tuesday, July 18th**

Floyd Landis

Temp: 90 °F / 32 °C Humidity: 60 % Heat Index: 99.7 °F / 37.6 °C

Stage Results: 187.0 km 38.3 km/hr 23.7 mph

Place: 4 Time: 4 hrs 53 min 32 sec Gap: 1 min 10 sec

GC Results: 2,629.0 km ridden 38.0 km/hr 23.5 mph

Place: 1 Time: 69 hrs 0 min 5 sec Gap: 0 hrs 0 min 0 sec

Race Notes: Floyd had the broken axle today and the mechanics forgot to switch out the computer with the wheel change. So we lost data.

This report is for the first 100 km and the other is calculated off of the math model.

Power, RPE, Heart Rate, Work, RPE vs. Power, HR vs. Power

		Power when Moving		Power when Pedaling		Strain		Work or Stress in Kjoules From:			RPE	HR
		Watts	Watts/kg	Watts	Watts/kg	RPE	HR	Power	RPE	HR	Pwr	Pwr
Rider	Today	270	3.94	321	4.65	**8**	**NA**	**4,755**	**6,804**	**NA**	**1.43**	**NA**
	Tour Avs						NA			NA		NA
	Tour Min	178	2.56	217	3.12	3.5	NA	2,624	2,682	NA	1.01	NA
	Tour Max	270	3.94	321	4.69	8	NA	5,870	7,619	NA	1.50	NA
2005	Today						NA			NA		NA
	Tour Avs	223	3.28	268	3.94	6.3	NA	3,911	5,348	NA	1.34	NA
	Tour Min	164 (S21)	2.41	214	3.15	4	NA	2,174 (S21)	2,651 (S21)	NA	0.88	NA
	Tour Max	285 (S11)	4.19	314	4.62	10 (S15)	NA	5,620 (S15)	11,286 (S15)	NA	2.01	NA

Power Distribution:

		Zero Watts		Per Kilogram of Body Weight																				Relative to RPE (1-10)					
				Time (%)										Time (min)										Time (%)			Time (min)		
		%	min	0-1	1-2	2-3	3-4	4-5	5-6	6-7	7-8	8-9	>9	0-1	1-2	2-3	3-4	4-5	5-6	6-7	7-8	8-9	>9	<H	H	>H	<H	H	>H
Rider	Today	15.3	39.0	18.5	6.7	10	15	18	13.2	8.5	4.7	2.4	2.5	47	17	25	39	46	34	22	12	6	6	51	31	18	128.5	79.5	46
	Tour Avs			23	12	14	14	14	11	6.28	2.95	1.4	1.3	68	35	41	42	43	34	18	8.4	3.9	3.7	63	25	12	185.8	76.28	34.35
	Tour Min	13.4	29.0	17.2	5.5	7.9	10	9.8	5.4	2.4	1.1	0.4	0.6	44	**17**	**25**	31	21	15	8.5	3.9	1.4	2.1	42	16.7	4.5	**129**	35.91	15.93
	Tour Max	23.9	80.0	30	19	19.3	18	24	21.3	9.4	**5**	**2.4**	**3**	101	57	68	64	89	78	29	**12**	**6**	**6**	78	45.5	16	276.5	166.5	47.95
2005	Today																												
	Tour Avs	15	41.2	20.4	11	12.4	14	16	14	7.22	2.91	1.2	1.1	55	29	34	38	45	40	20	8	3	3						
	Tour Min		26.0	12.6	5.7	6.9	11	9.1	6.8	3.7	1.7	0.9	0.7	37	16	19	26	20	15	8	4	2	2						
	Tour Max		84.0	33.8	16	16.8	17	23	27.9	10.3	4.7	1.7	1.7	104	42	46	48	73	85	31	14	5	5						

Peak Power Output: 5 min: ######## W/kg 30 min: ######## W/kg

		Average Power (watts)								Distance from Start (km)							
		Sec		Min				Hour		Sec		Min				Hour	
		5	30	1	5	10	30	1	2	5	30	1	5	10	30	1	2
Rider	Today								n								n
	Tour Avs	894	618	530	417	364	307	277	n								n
	Tour Min	825	528	471	340	296	252	214	n								n
	Tour Max	972	912	674	465	426	377	346	n								n
2005	Today																
	Tour Avs	841	555	479	400	360	314	283	255								
	Tour Min	731	465	403	308	283	249	231	193								
	Tour Max	965	645	555	478	435	386	359	315								

Surges:

		# of surges > than w/kg of:		
		> 6	> 8	> 10
Rider	Today			
	Tour Avs	381	107	31
	Tour Min	201	49	14
	Tour Max	**498**	**188**	**50**
2005	Today			
	Tour Avs			
	Tour Min			
	Tour Max			

Hydration & Energy Status:

Weight (kg)				Bottle	Sweat
Pre	Post	Δ	% Δ	Count	Loss (l)
69	68	1	1.4493	15	8.2
Est	Sweat Rates		%		
Loss (l)	l/hr	l/mjoule	GME	Kcals	
6.42	1.68	1.72	24	4733.0387	

Race Food Eaten:

Climbs and Special Features: Total Elevation Gain: 0 meter 0 feet Cr 0.005 k 0.18 Bike Wt 7 Wt 68.5 75.5

Climb/Feature:	Start (km)	Top (km)	Total Dist	% Grade	Calc Grade	Start Elev	Top Elev	Total Gain	Time Min	Time Sec	Speed km/hr	VAM m/hr	Estimated Power Roll	Aero	Grav	Total	Actual Power	W/kg	% Diff
1. Col de l'Izoard	71.8	86	14.2	7	6.9959308	1369	2360	991	40	23	21.09781	1472	22	37	310	369	342	4.92	7.437836622
2. Col du Lautaret*	121.9	134	12.1	4.4	4.40095	1526	2058	532	24	30	29.63265	1303	31	103	274	409	390	5.61	4.577309629
3. L'Alpe d'Huez	173.2	187	13.8	7.9	7.9013614	763	1850	1087	38	34	21.46932	1691	23	39	356	418	410	5.90	1.898626839
Actual time up L'Alpe																			
d'Huez. Time given by																			
official race course timers																			
who timed the climb.																			
* Time Estimated																			

Le Tour 2006: Daily Analysis Report

Stage 16: Bourg-D'Oisans to La Toussuire, 182 km *Wednesday, July 19th*

Floyd Landis

Temp: 90 °F / 32 °C Humidity: 60 % Heat Index: 99.7 °F / 37.6 °C

Stage Results: *182.0 km 31.5 km/hr 19.6 mph*

Place: 23 Time: 5 hrs 46 min 8 sec Gap: 10 min 4 sec

GC Results: *2,989.0 km ridden 40.0 km/hr 24.8 mph*

Place: 11 Time: 74 hrs 38 min 5 sec Gap: 0 hrs 8 min 8 sec

Race Notes: Bad Day. Floyd bonked on last climb. Didn't eat or drink enough. Missing last 6 km of Toussuire...

Power, RPE, Heart Rate, Work, RPE vs. Power, HR vs. Power

		Power when Moving		Power when Pedaling		Strain		Work or Stress in Kjoules From:			RPE	HR
		Watts	Watts/kg	Watts	Watts/kg	RPE	HR	Power	RPE	HR	Pwr	Pwr
Rider	Today	**259**	**3.73**	**312**	**4.48**	**10**	**NA**	**5,379**	**8,848**	**NA**	**1.64**	**NA**
	Tour Avs						NA			NA		NA
	Tour Min	178	2.56	217	3.12	3.5	NA	2,624	2,682	NA	1.01	NA
	Tour Max	267	3.84	314	4.52	7	NA	5,870	7,619	NA	1.50	NA
	Today						NA			NA		NA
	Tour Avs	223	3.28	268	3.94	6.3	NA	3,911	5,348	NA	1.34	NA
	Tour Min	164 (S21)	2.41	214	3.15	4	NA	2,174 (S21)	2,651 (S21)	NA	0.88	NA
	Tour Max	285 (S11)	4.19	314	4.62	10 (S15)	NA	5,620 (S15)	11,286 (S15)	NA	2.01	NA

Power Distribution:

		Zero Watts		Per Kilogram of Body Weight																				Relative to RPE (1-10)					
				Time (%)										Time (min)										Time (%)			Time (min)		
		%	min	0-1	1-2	2-3	3-4	4-5	5-6	6-7	7-8	8-9	>9	0-1	1-2	2-3	3-4	4-5	5-6	6-7	7-8	8-9	>9	<H	H	>H	<H	H	>H
Rider	Today	16.9	58.0	20.1	4.8	5.5	12	26	20.8	6.8	1.9	1.9	0	70	17	19	42	90	72	24	7	7	0	43	46.8	11	147.4	161.9	36.7
	Tour Avs																												
	Tour Min	13.4	29.0	17.2	5.5	7.9	10	9.8	5.4	2.4	1.1	0.4	0.6	44	20	29	31	21	15	8.5	3.9	1.4	2.1	42	16.7	4.5	154.5	35.91	15.93
	Tour Max	23.9	80.0	30	19	19.3	18	24	21.3	9.4	3.8	1.7	1.7	101	57	68	64	89	78	29	11	5	5	78	45.5	16	276.5	166.5	47.95
	Today																												
	Tour Avs	15	41.2	20.4	11	12.4	14	16	14	7.22	2.91	1.2	1.1	55	29	34	38	45	40	20	8	3	3						
	Tour Min		26.0	12.6	5.7	6.9	11	9.1	6.8	3.7	1.7	0.9	0.7	37	16	19	26	20	15	8	4	2	2						
	Tour Max		84.0	33.8	16	16.8	17	23	27.9	10.3	4.7	1.7	1.7	104	42	46	48	73	85	31	14	5	5						

Peak Power Output: 5 min: 5.94 W/kg 30 min: 5.23 W/kg

Surges:

		Average Power (watts)								Distance from Start (km)								# of surges > than w/kg of:		
		Sec		Min				Hour		Sec		Min				Hour				
		5	30	1	5	10	30	1	2	5	30	1	5	10	30	1	2	> 6	> 8	> 10
Rider	Today	828	722	478	406	378	358	344	n	136	27	21	20	159	20	20	n			
	Tour Avs								n								n			
	Tour Min	825	528	471	340	296	252	214	n								n	201	49	14
	Tour Max	972	912	674	465	426	377	346	n								n	487	141	43
	Today																			
	Tour Avs	841	555	479	400	360	314	283	255											
	Tour Min	731	465	403	308	283	249	231	193											
	Tour Max	965	645	555	478	435	386	359	315											

Hydration & Energy Status

Weight (kg)				Bottle Count	Sweat Loss (l)
Pre	Post	Δ	% Δ		
69	68	1	1.4493	20	10.6
Est Loss (l)	Sweat Rates l/hr		Sweat Rates l/mjoule	% GME	Kcals
7.27	1.84		1.97	24	5354.156713

Race Food Eaten:

Climbs and Special Features:

Total Elevation Gain: 0 meter 0 feet Cr 0.005 k 0.18 Bike Wt 7 Wt 68.5 75.5

Climb/Feature:	Start (km)	Top (km)	Total Dist	% Grade	Calc Grade	Start Elev	Top Elev	Total Gain	Time Min	Time Sec	Speed km/hr	VAM m/hr	Estimated Power Roll	Estimated Power Acro	Estimated Power Grav	Estimated Power Total	Actual Power	Actual w/kg	% Diff
1. Col du Galibier	2.7	45.5	42.8	4.5	4.5045632	720	2646	1926	96	32	26.60221	1197	28	75	252	355	333	4.79	6.12343085
2.Col de La Croix de Fer	103.8	126.5	22.7	6.9	6.8974059	505	2067	1562	67	33	20.16284	1387	21	33	292	346	334	4.81	3.432036413
3. Col du Mollard	140.7	146.5	5.8	6.8	6.8036233	1244.3	1638	393.7	16	29	21.11223	1433	22	37	302	361	348	5.01	3.680263055
4. La Toussuire	163	182	18.7	5.9	5.9033076	603	1705	1102	51	202	20.63765	1216	22	35	256	313	310	4.46	0.852670958
Toussuire first 3.12 km	163.3	166.416	3.116		7.7898956	603	845	242	8	59	20.81187	1616	22	36	340	398	382	5.50	4.018823171
Toussuire to 6.24 km	166.4	169.532	3.116		7.7251305	845	1085	240	9	51	18.98071	1462	20	27	308	355	342	4.92	3.642213029
Toussuire to 9.36 km	169.5	172.648	3.116		7.7251305	1085	1325	240	12	26	15.037	1158	16	13	244	273	269	3.87	1.531307335
Tousuire to 12.48 km	172.6	175.764	3.116		7.0779971	1325	1545	220	10	36	17.63774	1245	19	22	262	303	302	4.35	0.17772058
Toussuire to 15.60 km	175.8	178.88	3.116		2.7288717	1545	1630	85	6	30	28.76308	784.6	30	94	165	290		0.00	100
Tousuire to 18.72 km	178.9	181.996	3.116		2.4076295	1630	1705	75	6	0	31.16	750	33	120	158	311		0.00	100

Le Tour 2006: Daily Analysis Report

Stage 17: Saint-Jean-De-Maurienne to Morzine, 200.5 km **Thursday, July 20th**

Floyd Landis

Temp: 95 °F / 35 °C Humidity: 60 % Heat Index: 113 °F / 45.05 °C

Stage Results: 200.5 km 37.3 km/hr 23.0 mph

Place: 1 Time: 5 hrs 23 min 36 sec Gap: 0 min 0 sec

GC Results: 3,630.0 km ridden 33.7 km/hr 20.9 mph

Place: 3 Time: 80 hrs 9 min 19 sec Gap: 0 hrs 0 min 30 sec

Race Notes: The comeback kid.

Power, RPE, Heart Rate, Work, RPE vs. Power, HR vs. Power:

		Power when Moving		Power when Pedaling		Strain		Work or Stress in Kjoules From:			RPE	HR
		Watts	Watts/kg	Watts	Watts/kg	RPE	HR	Power	RPE	HR	Pwr	Pwr
Rider	Today	**281**	**4.16**	**324**	**4.80**	**10**	**NA**	**5,456**	**9,043**	**NA**	**1.66**	**NA**
	Tour Avs	226	3.27	274	3.95	5	NA	4,054	4,834	NA	1.16	NA
	Tour Min	178	2.56	217	3.12	3.5	NA	2,624	2,682	NA	1.01	NA
	Tour Max	281	4.16	324	4.52	10	NA	5,870	9,043	NA	1.66	NA
Team	Today						NA			NA		NA
	Tour Avs	223	3.28	268	3.94	6.3	NA	3,911	5,348	NA	1.34	NA
	Tour Min	164 (S21)	2.41	214	3.15	4	NA	2,174 (S21)	2,651 (S21)	NA	0.88	NA
	Tour Max	285 (S11)	4.19	314	4.62	10 (S15)	NA	5,620 (S15)	11,286 (S15)	NA	2.01	NA

Power Distribution:

		Zero Watts		Per Kilogram of Body Weight																				Relative to RPE (1-10)					
				Time (%)										Time (min)										Time (%)			Time (min)		
		%	min	0-1	1-2	2-3	3-4	4-5	5-6	6-7	7-8	8-9	>9	0-1	1-2	2-3	3-4	4-5	5-6	6-7	7-8	8-9	>9	<H	H	>H	<H	H	>H
Rider	Today	13.2	43.0	16.5	6.9	6.5	6.7	17	33.6	10.1	1.8	0.7	0.8	53	22	21	22	53	109	33	6	2	3	37	50	13	118.2	161.8	43
	Tour Avs	17.5	53.0	22.3	12	13.4	14	14	12.6	6.55	2.87	1.4	7.9	68	35	41	42	43	34	18	8	4	4	57	25	18	180.4	83	35.04
	Tour Min	13.4	29.0	17.2	5.5	7.9	10	9.8	5.4	2.4	1.1	0.4	0.6	44	20	29	31	21	15	8.5	3.9	1.4	2.1	42	16.7	4.5	154.5	35.91	15.93
	Tour Max	23.9	80.0	30	19	19.3	18	24	21.3	9.4	3.8	1.7	1.7	101	57	68	64	89	109	33	11	5	5	78	45.5	16	276.5	166.5	47.95
Team	Today																												
	Tour Avs	15	41.2	20.4	11	12.4	14	16	14	7.22	2.91	1.2	1.1	55	29	34	38	45	40	20	8	3	3						
	Tour Min		26.0	12.6	5.7	6.9	11	9.1	6.8	3.7	1.7	0.9	0.7	37	16	19	26	20	15	8	4	2	2						
	Tour Max		84.0	33.8	16	16.8	17	23	27.9	10.3	4.7	1.7	1.7	104	42	46	48	73	85	31	14	5	5						

Peak Power Output: 5 min 4.46 W/kg 10 min 5.97 W/kg

Surges:

		Average Power (watts)								Distance from Start (km)								# of surges > than w/kg of:		
		Sec		Min				Hour		Sec		Min				Hour				
		5	30	1	5	10	30	1	2	5	30	1	5	10	30	1	2	> 6	> 8	> 10
Rider	Today	867	544	484	451	431	401	352	n	9.6	69	71	70	69	69	154	n	564	67	22
	Tour Avs	894	618	530	417	364	307	277	n	146	133	122	81	115	119	74	n	381	107	31
	Tour Min	825	528	471	340	296	252	214	n								n	201	49	14
	Tour Max	972	912	674	465	**431**	**401**	**352**	n								n	**564**	141	43
Team	Today																			
	Tour Avs	841	555	479	400	360	314	283	255											
	Tour Min	731	465	403	308	283	249	231	193											
	Tour Max	965	645	555	478	435	386	359	315											

Hydration & Energy Status:

Weight (kg)				Bottle	Sweat
Pre	Post	Δ	% Δ	Count	Loss (l)
68	66.3	1.7	2.5	17	9.86
Est Loss (l)	Sweat Rates l/hr	Sweat Rates l/mjoule		% GME	Kcals
7.37	1.83	1.81		24	5430.801083

Race Food Eaten: 70 Bottles used. 15 to 20 used to drink. All others poured on himself during ride.

Climbs and Special Features:

Total Elevation Gain 0 meter 0 feet Cr 0.005 k 0.18 Bike Wt 7 Wt 67.15 74.15

Climb/Feature:	Start (km)	Top (km)	Total Dist	% Grade	Calc Grade	Start Elev	Top Elev	Total Gain	Time Min	Time Sec	Speed km/hr	VAM m/hr	Estimated Power Roll	Estimated Power Aero	Estimated Power Grav	Estimated Power Total	Actual Power	Actual w/kg	% Diff
1. Col des Saises	67.6	82.5	14.9	6.4	6.2335522	723	1650	927	36	55	24.2167	1507	25	56	317	399	395	5.68	1.015446223
2. Col des Aravis	103.1	109	5.9	7.1	7.1025934	1068	1486	418	16	49	21.05055	1491	22	37	314	373	371	5.34	0.584203133
3. Col de la Colombiere	122.2	134	11.8	5.8	5.7126887	940	1613	673	27	45	25.51351	1455	27	66	306	399	392	5.64	1.782191211
4. Cote de Chatillon-sur-Clus	156.9	162	5.1	4.9	4.9078609	485	735	250	11	7	27.52624	1349	29	83	284	396	374	5.38	5.507642235
5. Col de Joux-Plane	176.7	188.5	11.8	8.5	8.3424388	710	1691	981	37	34	18.8465	1567	20	27	330	376	372	5.35	1.142676113

Le Tour 2006: Daily Analysis Report

Stage 18: Morzine to Macon, 197 km — **Friday, July 21th**

Floyd Landis

Temp: 90 °F / 32 °C Humidity: 60 % Heat Index: 99.7 °F / 37.6 °C

Stage Results: 197.0 km 44.7 km/hr 27.7 mph

Place: 29 Time: 4 hrs 24 min 15 sec Gap: 8 min 0 sec

GC Results: 3,807.0 km ridden 33.2 km/hr 20.6 mph

Place: 3 Time: 84 hrs 33 min 34 sec Gap: 0 hrs 0 min 30 sec

Race Notes: Floyd just sitting in all day as breakaway with Levi and Z-man get away.

Power, RPE, Heart Rate, Work, RPE vs. Power, HR vs. Power

		Power when Moving		Power when Pedaling		Strain		Work or Stress in Kjoules From:			RPE	HR
		Watts	Watts/kg	Watts	Watts/kg	RPE	HR	Power	RPE	HR	Pwr	Pwr
Rider	Today						NA			NA		NA
	Tour Avs						NA			NA		NA
	Tour Min	178	2.56	217	3.12	3.5	NA	2,624	2,682	NA	1.01	NA
	Tour Max	267	3.84	314	4.52	7	NA	5,870	7,619	NA	1.50	NA
2006	Today						NA			NA		NA
	Tour Avs	223	3.28	268	3.94	6.3	NA	3,911	5,348	NA	1.34	NA
	Tour Min	164 (S21)	2.41	214	3.15	4	NA	2,174 (S21)	2,651 (S21)	NA	0.88	NA
	Tour Max	285 (S11)	4.19	314	4.62	10 (S15)	NA	5,620 (S15)	11,286 (S15)	NA	2.01	NA

Power Distribution:

		Zero Watts		Per Kilogram of Body Weight																				Relative to RPE (1-10)					
				Time (%)										Time (min)										Time (%)			Time (min)		
		%	min	0-1	1-2	2-3	3-4	4-5	5-6	6-7	7-8	8-9	>9	0-1	1-2	2-3	3-4	4-5	5-6	6-7	7-8	8-9	>9	<H	H	>H	<H	H	>H
Rider	Today																												
	Tour Avs																												
	Tour Min	13.4	29.0	17.2	5.5	7.9	10	9.8	5.4	2.4	1.1	0.4	0.6	44	20	29	31	21	15	8.5	3.9	1.4	2.1	42	16.7	4.5	154.5	35.91	15.93
	Tour Max	23.9	80.0	30	19	19.3	18	24	21.3	9.4	3.8	1.7	1.7	101	57	68	64	89	78	29	11	5	5	78	45.5	16	276.5	166.5	47.95
2006	Today																												
	Tour Avs	15	41.2	20.4	11	12.4	14	16	14	7.22	2.91	1.2	1.1	55	29	34	38	45	40	20	8	3	3						
	Tour Min		26.0	12.6	5.7	6.9	11	9.1	6.8	3.7	1.7	0.9	0.7	37	16	19	26	20	15	8	4	2	2						
	Tour Max		84.0	33.8	16	16.8	17	23	27.9	10.3	4.7	1.7	1.7	104	42	46	48	73	85	31	14	5	5						

Peak Power Output: 5 min: 0.00 w/kg 10 min: 0.00 W/kg

		Average Power (watts)								Distance from Start (km)							
		Sec		Min				Hour		Sec		Min				Hour	
		5	30	1	5	10	30	1	2	5	30	1	5	10	30	1	2
Rider	Today								n								n
	Tour Avs								n								n
	Tour Min	825	528	471	340	296	252	214	n								n
	Tour Max	972	912	674	465	426	377	346	n								n
2006	Today																
	Tour Avs	841	555	479	400	360	314	283	255								
	Tour Min	731	465	403	308	283	249	231	193								
	Tour Max	965	645	555	478	435	386	359	315								

Surges:

		# of surges > than w/kg of:		
		> 6	> 8	> 10
Rider	Today			
	Tour Avs			
	Tour Min	201	49	14
	Tour Max	487	141	43
2006	Today			
	Tour Avs			
	Tour Min			
	Tour Max			

Hydration & Energy Status:

Weight (kg)				Bottle Count	Sweat Loss (l)
Pre	Post	Δ	% Δ		
69	68	1	1.4493	20	10.6
Est Loss (l)	Sweat Rates			% GME	Kcals
	l/hr	l/mjoule			
0.00	2.41	#DIV/0!		24	0

Race Food Eaten:

Climbs and Special Features: Total Elevation Gain: 0 meter 0 feet Cr 0.005 k 0.18 Bike Wt 7 Wt 68.5 75.5

Climb/Feature:	Start (km)	Top (km)	Total Dist	% Grade	Calc Grade	Start Elev	Top Elev	Total Gain	Time		Speed km/hr	VAM m/hr	Estimated Power				Actual		% Diff
									Min	Sec			Roll	Aero	Grav	Total	Power	w/kg	

Le Tour 2006: Daily Analysis Report

Stage 20: Sceaux-Antony to Paris (Champs Elysees), 154.5 km ***Sunday, July 23rd***

Floyd Landis

Temp: 90 °F / 32 °C Humidity: 60 % Heat Index: 99.7 °F / 37.6 °C

Stage Results: *180.5 km 42.6 km/hr 26.4 mph*

Place: 30 Time: 4 hrs 14 min 30 sec Gap: 0 min 0 sec

GC Results: *3,807.6 km ridden 43.8 km/hr 27.1 mph*

Place: 1 Time: 64 hrs 6 min 33 sec Gap: 0 hrs 0 min 0 sec

Race Notes:

Power, RPE, Heart Rate, Work, RPE vs. Power, HR vs. Power

		Power when Moving		Power when Pedaling		Strain		Work or Stress in Kjoules From:			RPE	HR
		Watts	Watts/kg	Watts	Watts/kg	RPE	HR	Power	RPE	HR	Pwr	Pwr
Rider	Today						NA			NA		NA
	Tour Avs						NA			NA		NA
	Tour Min	178	2.56	217	3.12	3.5	NA	2,624	2,682	NA	1.01	NA
	Tour Max	267	3.84	314	4.52	7	NA	5,870	7,619	NA	1.50	NA
[illegible]	Today						NA			NA		NA
	Tour Avs	223	3.28	268	3.94	6.3	NA	3,911	5,348	NA	1.34	NA
	Tour Min	164 (S21)	2.41	214	3.15	4	NA	2,174 (S21)	2,651 (S21)	NA	0.88	NA
	Tour Max	285 (S11)	4.19	314	4.62	10 (S15)	NA	5,620 (S15)	11,286 (S15)	NA	2.01	NA

Power Distribution:

		Zero Watts		Per Kilogram of Body Weight																				Relative to RPE (1-10)					
				Time (%)										Time (min)										Time (%)			Time (min)		
		%	min	0-1	1-2	2-3	3-4	4-5	5-6	6-7	7-8	8-9	>9	0-1	1-2	2-3	3-4	4-5	5-6	6-7	7-8	8-9	>9	<H	H	>H	<H	H	>H
Rider	Today																												
	Tour Avs																												
	Tour Min	13.4	29.0	17.2	5.5	7.9	10	9.8	5.4	2.4	1.1	0.4	0.6	44	20	29	31	21	15	8.5	3.9	1.4	2.1	42	16.7	4.5	154.5	35.91	15.93
	Tour Max	23.9	80.0	30	19	19.3	18	24	21.3	9.4	3.8	1.7	1.7	101	57	68	64	89	78	29	11	5	5	78	45.5	16	276.5	166.5	47.95
[illegible]	Today																												
	Tour Avs	15	41.2	20.4	11	12.4	14	16	14	7.22	2.91	1.2	1.1	55	29	34	38	45	40	20	8	3	3						
	Tour Min		26.0	12.6	5.7	6.9	11	9.1	6.8	3.7	1.7	0.9	0.7	37	16	19	26	20	15	8	4	2	2						
	Tour Max		84.0	33.8	16	16.8	17	23	27.9	10.3	4.7	1.7	1.7	104	42	46	48	73	85	31	14	5	5						

Peak Power Output: 5 min 0.00 W/kg 10 min 0.00 W/kg — Surges: — Hydration & Energy Status:

		Average Power (watts)								Distance from Start (km)								# of surges > than w/kg of:		
		Sec		Min				Hour		Sec		Min				Hour				
		5	30	1	5	10	30	1	2	5	30	1	5	10	30	1	2	> 6	> 8	> 10
Rider	Today								n								n			
	Tour Avs								n								n			
	Tour Min	825	528	471	340	296	252	214	n								n	201	49	14
	Tour Max	972	912	674	465	426	377	346	n								n	487	141	43
[illegible]	Today																			
	Tour Avs	841	555	479	400	360	314	283	255											
	Tour Min	731	465	403	308	283	249	231	193											
	Tour Max	965	645	555	478	435	386	359	315											

Weight (kg)				Bottle Count	Sweat Loss (l)
Pre	Post	Δ	% Δ		
69	68	1	1.4493	20	10.6
Est Loss (l)	Sweat Rates		% GME	Kcals	
	l/hr	l/mjoule			
0.00	2.50	#DIV/0!	· 24	0	

Race Food Eaten:

Climbs and Special Features:

Total Elevation Gain: 0 meter 0 feet Cr 0.005 k 0.18 Bike Wt 7 Wt 68.5 75.5

Climb/Feature:	Start (km)	Top (km)	Total Dist	% Grade	Calc Grade	Start Elev	Top Elev	Total Gain	Time		Speed km/hr	VAM m/hr	Estimated Power				Actual		% Diff
									Min	Sec			Roll	Aero	Grav	Total	Power	w/kg	

ELSEVIER

Confirming testosterone administration by isotope ratio mass spectrometric analysis of urinary androstanediols

Cedric H.L. Shackleton,* Andy Phillips,† Tony Chang,* and Ye Li‡

**Children's Hospital Oakland Research Institute, Oakland, California, USA; †Micromass UK Limited, Manchester, England, UK; and, ‡National Research Institute of Sports Medicine, Beijing, China*

A gas chromatographic combustion isotope ratio mass spectrometric (GC/C/IRMS) method was used for studying the incorporation of exogenous testosterone enanthate into excreted urinary 5α- and 5β-androstane-3α,17β-diols. A multistep but straightforward work-up procedure produced a simple GC chromatogram of urinary steroid acetates composed principally of two androstanediols and pregnanediol. It is anticipated that such a method may form the basis of a doping control test for testosterone that could be used as a primary method during major sporting events or alternatively as a verification technique. Urine samples from five individuals were collected before and after administration of testosterone enanthate (250 mg). The $\delta^{13}C\ ^{0}/00$ *value of androstanediols was around −26 to −28 during the baseline period and decreased to about −29 to −30 in the days following synthetic testosterone administration. One of the other major steroids in the chromatogram, pregnanediol, was utilized as the "internal standard," because its* $\delta^{13}C^{0}/00$ *values did not markedly change following testosterone administration, remaining at −25 to −27. In all subjects studied, the* $\delta^{13}C^{0}/00$ *values for androstanediols were reduced sufficiently over 8 days to confirm administration of synthetic testosterone. Although steroids isolated from urine of normal individuals from 12 different countries gave values between −24 and −28, this seemed not to be related to nationality or region. The most likely variable is the proportion of plants with low and high carbon 13 content in the diet. This variable is likely to be more affected by individual food preferences than broad ethnic food divisions. In this paper, we propose a ratio of* $\delta^{13}C^{0}/00$ *for androstanediols to pregnanediol as a useful discriminant of testosterone misuse, a value above 1.1:1.0 being indicative of such misuse. The work-up procedure was designed for batch analysis and to use only simple techniques, rather than employ further instrumentation, such as high-performance liquid chromatography (HPLC), in purifying steroids for GC/C/IRMS. (Steroids* **62***:379–387, 1997) © 1997 by Elsevier Science Inc.*

Keywords: isotope ratio mass spectrometry (IRMS); doping control; testosterone

Introduction

The increasing need in sport for proving testosterone misuse requires new methodologies. For many years, a testosterone/epitestosterone (T/E) excretion ratio determined by gas chromatography–mass spectroscopy (GC–MS) of greater than 6:1 has been used as the hallmark for confirmation of drug administration,[1] but this method is fallible. For one thing, occasional drug-free individuals give a ratio >6, and a high ratio can also be adjusted downward by simultaneous administration of epitestosterone. We have found that in eight Chinese subjects given 250 mg testosterone enanthate, only three gave T/E values >6 on more than 1 day, demonstrating a high rate of false negatives, at least in this racial group.

In 1990, Southan and co-workers[2] used isotope ratio mass spectrometry (IRMS) to show that synthetic testosterone had a different ^{13}C content than endogenous hormone. This is a reflection of the origin of the materials, because all testosterone, both endogenous and synthetic, is ultimately of plant origin. Gonadal testosterone is made from precursor molecules derived from a wide variety of vegetable mate-

---

Address reprint requests to Cedric H.L. Shackleton, Children's Hospital Oakland Research Institute, 747 52nd Street, Oakland, CA 94609, USA.
Received July 25, 1996; accepted November 4, 1996.

Steroids 62:379–387, 1997

655 Avenue of the Americas, New York, NY 10010

0039-128X/97/$17.00
PII S0039-128X(96)00253-X

rials eaten by humans or by the animals humans eat. Individual plants discriminate to different degrees against $^{13}CO_2$, and particular species are known to have high or low levels of ^{13}C in their biomolecules.[3] In human bodies, the ^{13}C content, therefore, reflects an average of the ^{13}C content of all the plant material eaten by humans and our animal protein providers. Synthetic testosterone, in contrast, is generally made from a single plant species, mostly soy, so the ^{13}C content has a defined value reflecting the relatively low ^{13}C content of this plant. Thus, a significant difference in ^{13}C content between gonadal and soy testosterone could provide the basis for developing a definitive test for hormone misuse. Differences in carbon isotope ratios referred to by the symbol δ, defined as the difference in isotope ratio between the sample and an international carbonate standard "PDB." Although this is the accepted standard, for common usage a calibrated international standard of CO_2 is used. The values reported for δ carbon isotope ratios are

$$\delta^{13}C^{0}/_{00} = \left(\frac{\text{Ratio sample} - \text{Ratio PDB}}{\text{Ratio PDP}}\right) \times 1000$$

Becchi and coinvestigators have published pioneering studies on development of a method employing IRMS for determination of carbon isotope ratio of testosterone extracted from urine.[4,5] They demonstrated that, providing sufficient urine was available, the endogenous or exogenous origin of testosterone could be readily determined. A major remaining problem demonstrated by these studies relates to sensitivity of the analysis, because the quantity of urine collected from athletes is relatively small (about 75 mL), and this is divided into two, a primary (A) and a secondary sample (B). On each sample, nonsteroidal drug metabolites must be analyzed, as well as anabolic steroid screening and measurement of the T/E ratio.

We have attempted to improve the methodology to allow more sensitive analysis. It was decided to forgo any attempt to analyze testosterone itself and to concentrate on analysis of its metabolites 5α-androstane-3α,17β-diol (5αAD) and 5β-androstane-3α,17β-diol (5βAD). Our overall objective was to easily produce a single sample for analysis containing a few defined steroids to include the androstanediols and steroids we call "endogenous reference compounds" (ERCs). An ERC, in this instance, is a steroid whose carbon isotope ratio could not be altered through administration of exogenous testosterone. Aguilera, Becchi, and co-workers in their most recent publication use cholesterol and 5-androstene-3β,17β-diol as ERC.[5] To achieve our overall objective, we developed simple methodology adaptable to batch analysis, which required no liquid chromatographic (HPLC) instrumentation. Using this methodology, we determined the $\delta^{13}C^{0}/00$ of the androstanediols present in urine following administration of testosterone enanthate to five volunteers. This communication presents the results of this study.

Experimental

Materials

Testosterone enanthate, Testoviron depot® was obtained from Schering, Japan. Reference steroids were obtained from Sigma (St. Louis, Missouri, USA), which was also the supplier of Girard reagent T (carboxymethyl, trimethyl ammonium chloride hydrazide) and sodium bismuthate. Sephadex LH 20 was a product of Pharmacia AB and Sep-pak® cartridges, a product of Waters Corp. (Milford, Massachusetts, USA). β-glucuronidase/aryl sulfatase was obtained from Sigma (Type H1) and Boehringer Mannheim (Mannheim, Germany). Solvents were of analytical grade.

Individuals studied

Eight Chinese male subjects aged 19–22 were studied, although GC/C/IRMS analysis was only conducted on five. Permission for undertaking these experiments was obtained from the Chinese National Research Institute of Sports Medicine, and consent was obtained from the participants. Spot morning urine samples were collected for 2 days prior to an intramuscular injection of 250 mg testosterone enanthate. Two urine samples (0–8 h and 8–24 h) were collected for the first 4 days after administration, although only aliquots of the early morning sample were subject to analysis. Morning spot urine samples were collected on the 5–9th days after administration and on days 11, 13, and 15.

Determination of testosterone/epitestosterone ratio (T/E)

Urinary testosterone and epitestosterone were quantified in all the samples using an adaptation of the method of Donike et al.[6] These measurements were carried out by one of us (YL) in China at the National Institute of Sports Medicine. T/E ratios were then determined.

Preparation of steroid extract for GC/C/IRMS

A flowsheet summarizing the methodology is shown in Figure 1. Urine (typically 25 mL) was extracted by Sep-pak® cartridge according to the method of Shackleton and Whitney.[7] Once dried, the extract was dissolved in 3 mL 0.1 M acetate buffer pH 5 and *Helix pomatia*-derived β-glucuronidase/sulfatase (12 mg Sigma

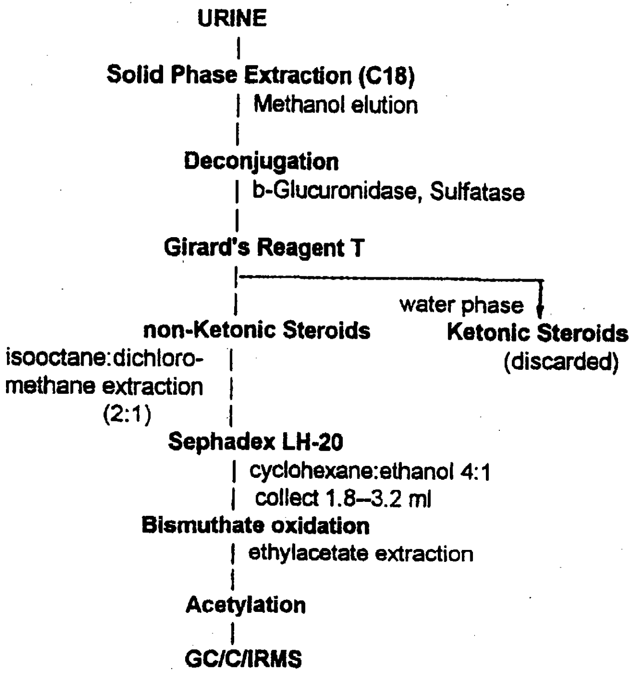

Figure 1 Flow sheet of the urinary extraction method.

type H1 powder, 100 μL Boehringer liquid enzyme) was added. Hydrolysis was allowed to proceed for 3 h at 55°C. A Girard separation was carried out to separate carbonyl-containing steroids (ketonic) from noncarbonyl-containing (nonketonic) steroids.[8,9] To the hydrolyzed urine mixture, 2 mL glacial acetic acid and 100 mg Girard reagent T was added. The solutions were placed in an oven at 100°C for 30 min. The nonketonic steroids were extracted by 2 × 5 ml isooctane: dichloromethane 2:1 (v/v), and the solvent was dried. Small columns of 0.5 Sephadex LH-20 were prepared in Pasteur pipettes, the Sephadex being allowed to swell in the cyclohexane: ethanol (4:1) solvent system before preparation.[10] The steroid extract dissolved in 100 μL of the same solvent mixture was added to these columns. Solvent eluting between 1.8 and 3.2 mL was collected and dried. Acetic acid (0.1 mL), water (0.1 mL), and 5 mg sodium bismuthate were added.[9] Oxidation was allowed to proceed for 2 h, and after neutralization (0.5 mL of 0.5 M acetate buffer), the mixture was extracted with 4 mL ethyl acetate. After drying, steroid acetates were prepared overnight with 50 μL acetic anhydride and 50 μL pyridine. The acetates were analyzed by GC/C/IRMS.

Gas chromatography combustion isotope mass spectrometry (GC/C/IRMS)

A schematic representation of the GC/C/IRMS instrumentation is illustrated in Figure 2. The acetylated steroid samples were kept refrigerated until analysis. Cyclohexane (20 μL; 99.9% pure from Sigma Chemicals 27-0625-8) was added to each vial, and one-tenth (2 μL) of each sample was injected splitless onto a J&W 30 m DB17 capillary column housed in a Fisons 8000 series GC. The injector was kept at 220°C. The temperature program was as follows: starting temperature 50°C (1 min), followed by rapid temperature increase (25° min) to 300°C, where it was held for 15 min.

The separated components were heart-split into the combustion furnace filled with copper oxide wires (Elemental Microanalysis Limited, UK) held at 850°C. The combustion gases were passed through a nafion membrane water removal trap, and the remaining CO_2 was analyzed on a Micromass isochrom isotope mass spectrometer. The mass spectrometer consisted of an electron impact source running at 400 μA trap current, the ionized CO_2 gas, was focused by a magnet onto three Faraday collectors. The ions collected were those at masses 44, 45, and 46. The Micromass data system calculated the areas of the beams and subtracted any background; whereupon, calculation of the ^{13}C δ values for the successive peaks were carried out.

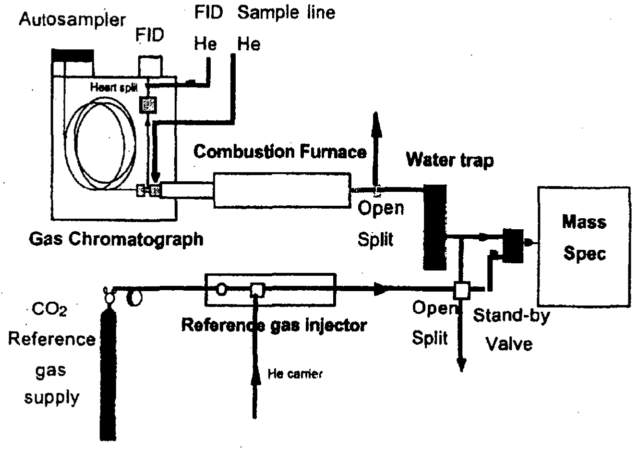

Figure 2 Schematic of the Micromass GC/C/IRMS instrument.

Results and discussion

Evaluation of gas chromatographic columns

The objective of the study was to measure $\delta^{13}C^0/00$ for urinary androstanediols formed as metabolites of testosterone. In our initial studies (Subject 1), we undertook chromatography on DB1 capillary columns but did not get resolution of the two diacetylated epimers (Figure 3A). Later employment of a DB17 column (Figure 3B) allowed separation of the epimers as well as the ERC, pregnanediol diacetate, and pregnanetriol diacetate (Figure 3B).

Confirmation of identity of steroids in extracts

Prior to sending the first samples for GC/C/IRMS analyses in England, the identities of the principal components of the chromatogram were confirmed by GC/MS. This was carried out on a Hewlett-Packard 5970 instrument housing a 15 meter DB1 capillary column. The peaks chosen for GC/C/IRMS analyses had retention times and electron impact mass spectra identical to those of 5α- and 5β-androstanediol diacetate and pregnanediol diacetate. Reference steroids for these compounds were also analyzed on the GC/C/IRMS instrument using both DB1 and DB17 columns, and these gave identical retention times to the urinary steroids. Pregnanetriol could also be analyzed by GC/C/IRMS.

Achievement of work-up procedure objective

The method developed and utilized had the following qualities. First, the Girard separation almost completely removed carbonyl containing steroids from the hydrolyzed extracts, which probably represent 75% of urinary steroids. Exceptions may be the 11-carbonyl containing steroids that probably do not react because of the hindered nature of that functional group. Second, a crude micro Sephadex LH-20 column separation effectively produced a fraction containing steroids with two and three functional groups. Third, sodium bismuthate oxidation was designed into the procedure as a means of removing remaining long-retention time pregnane metabolites, thus allowing shorter periods between injection. Many of the quantitatively more important metabolites are converted into 17-oxygenated C_{19} steroids by the procedure. Fourth, acetylation provided steroids with good gas chromatographic properties that were readily separated. Fifth, despite the complexity of the steroid fraction of urine, the final chromatogram was simple and composed of only a few peaks for which $\delta^{13}C^0/00$ could be determined with accuracy.

$\delta^{13}C^0/00$ value of the synthetic testosterone

Testosterone acetate prepared from the Japanese testosterone enanthate used for injection in these studies gave a $^{13}C^0/00$ value of −30.41, a value close to the lowest value obtained for androstanediol diacetate measurements obtained in the subjects studied following testosterone administration.

We also analyzed five other current products and one synthetic sample made more than 40 years ago. The following results were obtained: testosterone of Chinese manufacture −30.40; U.S. manufacture −30.38; two Czech products,